PATENT SPECIFICATION

DRAWINGS ATTACHED

Inventors: JERZY KONRAD SKREBOWSKI and JOHN WILLIAMSON

1,159,670

1,159,670

Date of Application and filing Complete Specification: 26 Jan., 1967.
No. 3960/67.
Complete Specification Published: 30 July, 1969.

Index at acceptance:—C5 E(7B1A2, 7B1Y, 9B1); B1 GX

Int. Cl.:—C 07 c 7/14, 15/08

COMPLETE SPECIFICATION

Refrigeration Process

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London S.W.1. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly descrabed in and by the following statement:—

THIS INVENTION is concerned with a refrigeration process.

In processes for freezing liquids, for example those comprising paraxylene and at least one other xylene and/or ethyl benzene, to produce slurries comprising a mother liquor and crystals, by contacting them with a cold surface, there is a tendency to build up solid deposits on the chilled surface, which results in inefficient heat transfer and failure to recover the crystal products rapidly from the system. It has previously been proposed to provide mechanical scrapers to clean the chilled surface, but such systems are often expensive to maintain and produce slurries containing mainly small crystals especially in the case of paraxylene crystals. We have now devised means whereby this problem may be significantly reduced.

According to our British complete specification in Patent Application Nos. 35367/65, 9187/66 and 29226/66 (Serial No. 1104508) this difficulty may be overcome, when p-xylene slurries are produced, by subjecting the chilled surface to sonic vibrations. This is a most effective procedure, but suffers from the disadvantage that sonic vibrations are easily lost from the surface to parts of the apparatus by which it is supported, and it is normally necessary to isolate the surface accoustically.

The present invention is based on the discovery that crystals may be very effectively dislodged from the chilled surface by subjecting the liquid undergoing chilling by contact with the surface to sonic vibrations, and that such vibrations largely "bounce off" i.e. are reflected from, the surface, which therefore need not vibrate to a sufficient extent to render acoustical isolation necessary.

The invention therefore provides a process of freezing a liquid to produce a slurry comprising crystals and mother liquor which comprises contacting the liquid with a cold surface at a sufficiently low temperature to cause the formation of crystals on the cold surface and detaching crystals from the cold surface by applying sonic vibrations to the liquid at a point removed from the cold surface. (The term "sonic vibrations" in this application includes vibrations above the audible range.) The frequency of the vibrations is at least 40 cycles per second and is preferably in the range of 0.5 to 100 kilocycles per second. Suitably, vibrations of a low frequency of from 5, and preferably 10, to 30 kilocycles per second are used as these tend to produce a high turbulence in the layer of liquid close to the cooling surface and tend also to be easily produced at a high power.

The invention also provides apparatus for carrying out the said process.

It is preferred to apply the vibrations at a small angle of at most 20° to the cold surface, so as to increase the proportion of the vibrations reflected. It is especially preferred that the vibrations should be parallel to the surface. We have found the use of such small angles to be very effective in preventing incrustation of the cold surface.

The invention is especially suitable for producing slurries from liquids which are mixtures of organic compounds. It is preferred, when the liquid comprises paraxylene that it should comprise at least 10% and preferably at least 15%, to 85% by

weight of paraxylene, the remainder of the liquid comprising one or more other xylenes and/or ethyl benzene.

The cold surface is a thermally conductive barrier preferably separating the liquid to be chilled from a refrigerant.

We have found that the process of this invention permits at the same rate of heat exchange and under the same process conditions, the production of larger crystals than is possible if only mechanical scraping is used to free the surface of crystal deposits. We have also found that a higher rate of heat exchange can be achieved with the same temperature difference between the chilled surface and the liquid.

Suitable cold surfaces may be provided, for example, by using one or more tubes of which the walls form thermally conductive barriers, the said tubes either conducting the liquid to be chilled through a bath of refrigerant or conducting a refrigerant through a vessel containing the liquid to be chilled. Such tubes should preferably have an internal diameter of not less than one quarter and more preferably not less than half an inch.

Plate and corrugation heat exchangers may also be used.

A particularly satisfactory form of this invention is obtained by providing a second surface facing the cold surface the liquid being between the said surfaces, and transmitting sonic vibrations substantially parallel to the cold surface. The second surface to reflect diverging sound waves onto the cold surface. The second surface mày itself be a cold surface in order to increase the total freezing effect, but a highly efficient process may be obtainıd without this.

One apparatus according to the invention comprises two, preferably substantially concentric, straight tubes one of which contains the liquid to be frozen and the other of which contains refrigerant, and means to apply through the liquid to be frozen, sonic vibration longitudinally to the cold surface contacting the liquid to be frozen, the inner tube being of thermally conductive material. The outer tube very suitably contains the liquid to be frozen. The inner tube may be closed at one end, thus forming a finger, or may be open at both ends. If a finger is used and the vibration is transmitted from beyond the closed end it is preferred that the closed end should be pointed, as we have found that flat or rounded ends tend to ice up, whereas pointed ends are not only more satisfactory in this respect, but the vibrations reflected from them are re-reflected from the outer cylindrical tube and exercise a de-icing effect further up the finger. It is, however not essential to have a pointed end, and for ease of fabrication, rounded or flat ends may be preferred.

An advàntage of the use of a finger is that the sonic vibrations need be generated over a small cross-sectional area only, being directed towards the end of the finger, whereas with tubes of which both ends are open it is desirable to provide an annular sonic vibrator or several individual sonic vibrators round the tube so as to avoid "shadowing" of parts of the cold surface.

A finger may if desired be secured rigidly at its open end, suitably by means of a flange, to other parts of the apparatus, for example the vessel containing liquid undergoing treatment . The finger may be fed with refrigerant, if a downwardly extending finger is used, by uniting the open end of the finger to a refrigerant reservoir.

The refrigerant may be pumped to the closed end of the finger through an internal tube, but this normally unnecessary with downwardly extending fingers as, if the tube has a sufficient diameter (for many purposes an internal diameter of 4 inches is ample if the finger is, for example, five feet long), liquid refrigerant flows into the tube under the influence of gravity at a quite satisfactory rate despite the effect of boiling.

One suitable form of apparatus according to the invention comprises a bath for the liquid to be frozen, a plurality of cylindrical fingers dipping into the bath, the fingers being either close together and parallel so that sonic vibrations are reflected from one to another or being surrounded by cylindrical sheats substantially concentric with and spaced away from the fingers, and at the base of the bath sonic vibrators directed towards the base of the fingers. Alternatively, for ease of construction, flat separators may be provided in the liquid between the fingers.

Refrigerànts for cooling the chilled surface may be cooled in any refrigeration device, which may be of conventional design. The refrigerant may be for example, ammonia, ethylene, ethane or carbon dioxide. Suitable refrigerants however when only moderately decreased temperatures are required are brine, petrol, methanol and acetone, or preferably a pentane, for example n-pentane.

A number of the refrigerants for chilling the surface (for example ammonia, ethylene, ethane and carbon dioxide) normally evaporate in the chilling process, and thus produce a "boiling" effect, though this can be suppressed by using high pressures. Refrigerants of this type are particularly appropriate for the production of low temperatures, which are used in the treatment of mixtures of xylenes (which may contain ethyl benzene) containing only small concentrations (for example, of 10%—30%, and more usually 15%—25% by weight) of p-xylene.

The formation of p-xylene crystals occurs satisfactorily on flat, concave or convex surfaces.

Suitable chilled surfaces are of any

material resistant to the temperatures employed in the process, which has a high thermal conductivity, for example, aluminium and its alloys, many copper alloys especially the copper/beryllium alloys and brass, but preferably steels, for example stainless steel. Preferably, the surface is smooth, and it is more preferably polished.

The source of the sonic vibrations may be for example a piezo electric device, a liquid siren or a generator for electric current at a frequency of from 0.5 to 100 kilocycles per second, together with a coil connected across the generator and surrouding a core of magneto-strictive material, one end of the core being contacted either directly or indirectly, for example through a velocity transformer to amplify the vibrations, with the liquid to be frozen.

Preferably the sonic vibrations have a power of, for example, 5 to 200 watts per square foot of the cold surface.

At least 10 watts per square foot and at most 100 watts per square foot are usually used.

The cold surface may be at a temperature in the range of 0.5 to 30 or even 50 Centigrade degrees and preferably 5 to 20 Centigrade degrees below the temperature of crystallisation of the liquid. A preferable temperature difference is 10 to 15°C. In general, the freater the temperature difference, the greater the power of sonic vibration required. The greater the concentration of p-xylene in mixtures comprising at least one other xylene and/or ethyl benzene, the smaller the temperature difference which is practical.

It is preferred that the process of the invention be carried out whilst feeding the liquid and withdrawing the slurry continually.

The liquid to be frozen may if desired be stirred, but it is more preferably pumped past the cold surface.

It is preferred that the linear flow rate should be at least six inches per second, and that flow should be turbulent. If a liquid siren is used as a sonic vibrator it has the advantage of creating its own turbulence.

It is advantageous to pass the slurry produced into a settling tank so as to permit the withdrawal of a thickened slurry from the base and to allow any possible increase in crystal size thus facilitating subsequent separation of the crystals. At least part of the thinner part of the slurry in the settling tank may be recycled to the liquid contacting the cold surface so as to "seed" the liquid and thus further to increase the crystal size.

Intermittent sonic vibrations may be applied according to the invention but it is preferred to apply them continously during the process in order to prevent the build up of incrustations.

By the use of this process slurries containing 50% or more by weight of solids may be produced, though for handling purposes slurries containing at most 40%, for example 5 to 25% by weight of solids are normally preferred.

In all forms of the invention it is preferred when the weight of vibrating parts of the apparatus is supported rigidly, to provide the support at nodal points, if such points exist.

The crystallised material may be recovered by any suitable method, for example, by filtering or centrifuging the slurry to separate the crystals, or the slurry may be treated in known manner to recover the crystallised material as a liquid by for example feeding the slurry to a pulsed column apparatus of conventional type such as that as described by Marwil and Kolmer, Chemical Engineering Progress 59 (February 1963) page 60.

Example 1

The apparatus will now be described with reference to the Drawing.

A three inch external diameter, 13½ inch long stainless steel round bottomed tube (1) was mounted in a 4" internal diameter glass column (2) holding a mixture of xylenes and ethyl benzene containing 70% by weight of paraxylene. 9½ inches of the tube were immersed in the mixture. A 2" diameter velocity head (3) was fixed at its nodal (mid) point in the base of the glass column so that the free end faced the bottom of the tube and was 4½ inches from it. A thermometer (7) was provided dipping into the liquid mixture, and tubes (5) and (6) were provided for circulating (if required) liquid through the glass column. The velocity head (3) was vibrated at 13 kilocycles/sec. by three magnetostrictive transducers (4) driven by a nominal 100-watt electrical generator. No attempt to optimise the efficiency of conversion of electrical to mechanical energy was made. Cold methanol was circulated through the tube by means of pipes (8) and (9), a constant depth of methanol of 9½" being maintained in the tube.

With the xylenes unagitated, and at a heat flux of 350 kilocalories/hr./sq.ft. (corresponding to the maximum refrigeration capacity for the cold methanol), using sonic vibrations, no ice adhered to the surface of the tube. A slurry containing 18% by weight of paraxylene crystals was produced.

Without sonic vibrations the tube iced up as soon as the freezing point of the liquid was reached. The above procedure was repeated, circulating the mixture of xylenes and ethyl benzene through the glass column through pipes (5) and (6). Slurry formation was possible without forming surface ice up to a heat flux of 450 kilocalories/sq.ft./hr. using sonic vibrations. Without vibrations,

the maximum heat flux which did not cause icing up was 90 kilocalories/hr./sq.ft.

Example 2

The apparatus used in this experiment was similar to that of Example 1, except that nozzles were provided through which the inner walls of the tube were sprayed with acetone and a vacuum was applied to the inside of the tube to evaporate the acetone. The mixture of xylenes and ethyl benzene was again circulated, No icing of the tube surface was observed at a heat flux of 470 kilocalories/sq.ft./hr. using sonic vibrations as before.

Without sonic vibrations the maximum allowable heat flux was 80 kilocalories/sq.-ft./hr.

Example 3

The tube of example 2 was filled to a depth of 9½" with a commercially available refrigerant boiling at a temperature of —30°C. at atmospheric pressure and sold under the trade mark "Arcton" 12. The refrigerant was then allowed to boil. The maximum heat flux without icing up using sonic vibrations was 480 kilocalories/sq.ft./hr. and the maximum heat flux without the vibration was 100 kilocalories/sq.ft./hr,. the mixture of xylenes and ethyl benzene being circulated in both cases.

On repeating this procedure using a 6" nominal bore glass column, the end of the tube being 4½ inches from the end of the velocity head, the maximum heat flux with the sonic vibrations was 470 kilocalories/sq.-ft./hr. and without the vibration, 80 kilocalories/sq.ft./hr.

Using a 6" nominal bore glass column with the end of the tube 17" from the velocity head, the maximum allowable heat flux with the sonic vibration was 400 kilocalories/sq.-ft./hr. and without the vibration was 90 kilocalories/sq.ft./hr.

WHAT WE CLAIM IS:—

1. A process of freezing a liquid to produce a slurry comprising crystals and mother liquor which comprises contacting the liquid with a cold surface at a sufficiently low temperature to cause the formation of crystals on the cold surface and detaching crystals from the cold surface by applying sonic vibrations to the liquid at a point removed from the cold surface.

2. A process as claimed in Claim 1 in which the vibrations have a frequency in the range of from 0.5 to 100 kilocycles per second.

3. A process as claimed in Claim 2 in which the vibrations have a frequency of from 5 to 30 kilocycles per second.

4. A process as claimed in Claim 1, 2 or 3 in which the vibrations are applied at an angle of at most 20° to the cold surface.

5. A process as claimed in Claim 4 in which the vibrations are substantially parallel to the surface.

6. A process as claimed in any preceding claim in which the liquid is a mixture of organic compounds.

7. A process as claimed in Claim 6 in which the liquid comprises from 10 to 85% of paraxylene by weight, the remainder of the liquid comprising one or more other xylenes and/or ethyl benzene.

8. A process as claimed in any preceding claim in which the cold surface is a thermally conductive barrier separating the liquid to be chilled from a refrigerant.

9. A process as claimed in Claim 8 in which the cold surface is provided in the form of one or more tubes of which the walls form thermally conductive barriers, the said tubes either conducting the liquid to be chilled through a bath of refrigerant or conducting a refrigerant through a vessel containing the liquid to be chilled.

10. A process as claimed in any preceding claim in which a second surface faces the cold surface, the liquid being between the said surfaces, and in which sonic vibrations are transmitted substantially parallel to the cold surface.

11. A process as claimed in Claim 10 in which the second surface is itself a cold surface.

12. A process as claimed in any preceding claim in which the liquid is fed and the slurry is withdrawn continuously.

13. A process as claimed in any of Claims 1—12 in which a refrigerant which evaporates during the chilling process is employed for chilling the surface.

14. A process as claimed in any of Claims 1—13 in which the sonic vibrations have power of 5 to 200 watts per square foot of the cold surface.

15. A process as claimed in Claim 14 in which the sonic vibrations have the power of 10 to 100 watts per square foot of the cold surface.

16. A process as claimed in any of Claims 1—15 in which the temperature of the cold surface is in the range of 0.5 to 30 Centigrade degrees below the temperature of crystallisation of the liquid.

17. A process as claimed in Claim 16 in which the temperature of the cold surface is 10 to 15 Centigrade degrees below the temperature of crystallisation of the liquid.

18. A process as claimed in any of Claims 1—17 in which the liquid to be frozen is stirred, or pumped past the cold surface.

19. A process as claimed in Claim 18 in which a liquid siren is used as a sonic vibrator.

20. A process according to any of Claims 1—19 in which the slurry produced is passed into a settling tank so as to permit the

withdrawal of a thickened slurry from the base thereof, at least part of the thinner part of the slurry recovered from the settling tank being recycled to the liquid contacting the cold surface.

21. A process as claimed in any of Claims 1—20 in which the sonic vibrations are applied continuously during the process.

22. A process for freezing a liquid to produce a slurry whenever carried out substantially as described in the Examples.

23. Crystallised material whenever produced by the process as claimed in any of Claims 1—22.

24. Apparatus suitable for freezing a liquid to produce a slurry of crystals in mother liquor which comprises an inner straight tube of thermally conductive material for containing liquid or refrigerant, an outer tube disposed substantially concentrically around the inner tube to provide an annular space for containing liquid or refrigerant and means to apply sonic vibrations to liquid in a longitudinal direction with relation to the tubes.

25. Apparatus as claimed in Claim 24 in which the outer tube is adapted to contain the liquid to be frozen.

26. Apparatus as claimed in Claim 25 in which the inner tube is closed at one end to form a finger.

27. Apparatus as claimed in Claim 26 in which means is provided for transmitting sonic vibrations from beyond the closed end of the finger and in which the closed end is pointed.

28. Apparatus as claimed in any of Claims 24—27 in which the finger is secured rigidly at its open end to other parts of the apparatus.

29. Apparatus as claimed in Claim 28 in which the finger extends downwardly and the open thereof is united to a refrigerant reservoir.

30. Apparatus for carrying out a process as claimed in any of Claims 1—23 which comprises a bath for the liquid to be frozen, a plurality of cylindrical fingers dipping into the bath which are either situated close together and parallel to one another or which are surrounded by cylindrical sheaths substantially concentric with and spaced away from the fingers, and at the base of the bath sonic vibrators directed towards the base of the fingers.

31. Processes for freezing liquids as claimed in any of Claims 1—22 whenever carried out in an apparatus according to any of Claims 24—30.

WALTER SCOTT,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2. from which copies may be obtained.

1,159,670 COMPLETE SPECIFICATION

I SHEET This drawing is a reproduction of the Original on a reduced scale.